

# THE GEOCHEMISTRY OF SULPHUR IN A MIXED ALLOGENIC–AUTOGENIC KARST CATCHMENT, CASTLETON, DERBYSHIRE, UK

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## ABSTRACT

Analyses are presented of anion chemistry and sulphur isotopic compositions of sulphate in sinking streams and groundwaters in a mixed allogenic–autogenic karst catchment. Using the sulphur isotopic data, sources of sulphate from agriculture and the effects of sulphate reduction arising from slurry application can be distinguished from natural rock weathering sources. Within the aquifer, sulphate in known autogenic waters has isotopic compositions distinct from allogenic waters, the autogenic waters being dominated by sulphate from rainfall and rock weathering in these low agricultural intensity catchments. On this basis, water rising at low flow from Whirlpool Rising, Speedwell Cavern, has been identified as dominantly autogenic.

Groundwater flow between the sinks and risings in Speedwell Cavern is believed to be along conduits following mineralized faults (rakes). During transit  $\text{SO}_4^{2-}/\text{Cl}^-$  in the water increases. Isotopic mass balance shows that this must be due to addition of sulphate from the oxidation of ore minerals by groundwater. Mass balance considerations show that the present rate of sulphide oxidation must be the result of enhancement by lead mining operations on the rakes. Copyright © 2000 John Wiley & Sons, Ltd.

## INTRODUCTION

Sulphate is a ubiquitous component of the solute load of natural waters. It is a significant anion in precipitation and is augmented in surface- and groundwaters by a variety of sources and processes, both natural and anthropogenic. All natural sulphur consists predominantly of two stable isotopes,  $^{32}\text{S}$  (95 per cent) and  $^{34}\text{S}$  (4.2 per cent), and their relative abundance is variable due to isotopic fractionation associated with natural processes. Thus different sources of sulphur may be characterized by different isotopic compositions, and hence different sources of sulphate to waters in a catchment might be distinguished by their isotopic composition. Since sulphur is associated with many anthropogenic sources of solute (e.g. acid rain and agrochemicals) as well as natural weathering reactions, study of the isotopic composition of sulphate sulphur may potentially be used to construct catchment budgets for these different sources of sulphate. In this study we use isotopic techniques to distinguish sulphur sources and processes affecting the hydrochemistry of sulphur in a mixed allogenic–autogenic karst catchment in central England, which is influenced by both natural and anthropogenic processes.

### *Geology and hydrology of the catchment*

The Castleton karst catchment lies in the northeast of the Derbyshire Peak District and covers an area of approximately 13.5 km<sup>2</sup> (Figure 1). The aquifer is developed in Carboniferous (Dinantian) limestones that are overlain, locally unconformably, by the Namurian Edale Shales. Thinly bedded and commonly pyritic marine muds and silts of early Namurian age grade upward to massively bedded sands of Millstone Grit facies. Following deformation, which produced a broadly dome-like structure cored by the limestone, lead–zinc

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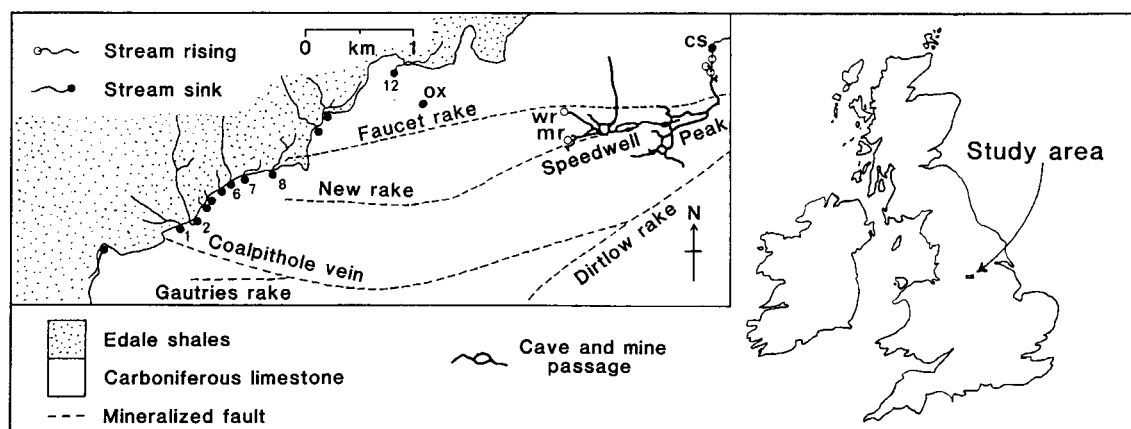


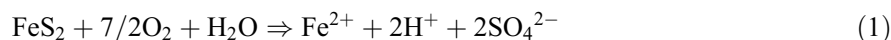
Figure 1. Simplified geology and hydrology of the Castleton karst catchment. mr = Main Rising; wr = Whirlpool Rising; the combined flows of resurgences at Peak Cavern, Slop Moll and Russet Well form the Castleton water (cs) referred to in the text. ox is the location of the Oxlow House borehole. Numbered stream sinks correspond to P1, P2, etc. in the text

mineral veins ('rakes') were emplaced along fractures in the limestone (Worley and Ford, 1977; Ineson and Ford, 1982). These partially mineralized fractures within the limestones of the catchment exert significant influence on the hydrogeology of the area. In the western part of the area the shale/limestone contact is obscured by Quaternary deposits, which form a flat floor to a valley between hills formed in Namurian shales and sandstones (Rushup Edge) to the north and Dinantian limestones to the south.

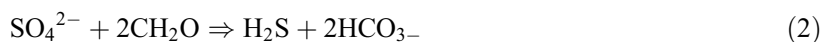
A limestone area of approximately 8.5 km<sup>2</sup> is drained by three springs in Castleton village, and this water is supplemented by run-off from 5 km<sup>2</sup> of Namurian shales and sandstones on Rushup Edge. Water flowing from Rushup Edge forms streams that flow across a flat-floored valley and cut small gorges into the Quaternary sediments before sinking into a number of swallets, just after crossing onto the limestone. The sinking allogenic water then drains to the Peak–Speedwell Cavern system, probably via a series of conduits developed within mineralized fault zones (Ford, 1966; Gunn, 1991). Dye tracing shows that the allogenic waters emerge in Speedwell Cavern at two points, Main Rising (MR) and Whirlpool Rising (WR). Whereas it is known that the dominant flow can switch between risings (Bottrell and Gunn, 1991), during this study the major flow was always from Main Rising. Throughout the catchment, autogenic percolation waters augment the allogenic drainage and a component of the flow at Main Rising is of autogenic origin. Further autogenic water is added from Cliff Cavern (CC), Boulder Piles (BP) and other minor percolation water inlets in the Speedwell Cavern system. The sizes of the autogenic catchments are difficult to estimate, but that of Main Rising is unlikely to be greater than 1 km<sup>2</sup> (compared to the allogenic catchment of 5 km<sup>2</sup>). Thus, the water emerging from Main Rising is more than 80 per cent allogenic. Under all flows the combined waters flow through a vadose streamway in Speedwell Cavern before entering a phreatic conduit to re-emerge at Slop Moll and Russet Well. Under high flows, water from the Speedwell system overflows into Peak Cavern, but at other times the water in Peak Cavern is entirely autogenic, the main inputs being via Far Sump and Ink Sump. The water emerges at Peak Cavern Rising, which is some 50 m upstream of Slop Moll.

#### *Potential sources and sinks for aqueous sulphate*

Autogenic recharge to the limestone aquifer is from rainfall which is influenced by atmospheric pollutants. In the surface catchment underlain by Namurian shales, pyrite oxidation is known to be a significant process in weathering of bedrock (Vear and Curtis, 1981) and will release sulphate to surface streams which drain these hillsides and provide allogenic recharge to the aquifer:



Pyrite is also present, but at far lower concentrations (see below), in the limestones of the catchment and provides an additional potential sulphate source. Most of the catchment is farmland, though the intensity of agriculture is variable with some areas largely unimproved. Agricultural practices and soil zone processes may further modify sulphate concentrations and isotopic compositions. Many agrochemicals and slurries/sludges applied as fertilizers contain significant amounts of sulphate (applications of which can be large compared to the precipitation inputs). These sources may supply additional sulphur to surface waters which sink as allogenic inputs or, on the limestone catchments, directly to infiltrating autogenic percolation waters. However, in organic-rich soils or soils with a high organic input as slurries, sulphate in soil waters can be consumed by bacterial sulphate reduction (BSR) (McCarthy and Bottrell, 1999). This proceeds only in anoxic environments, where sulphate-reducing bacteria use sulphate as a terminal electron acceptor (oxidizing agent) in the metabolism of organic carbon:



This reaction carries a characteristic isotopic fractionation, the bacteria preferentially processing the lighter  $^{32}\text{S}$  isotope (Nakai and Jensen, 1964; Chambers and Trudinger, 1979). Thus as the sulphate concentration decreases, the residual sulphate becomes enriched in the heavier  $^{34}\text{S}$  isotope as isotopically light  $\text{H}_2\text{S}$  is formed (and is fixed in the soil as pyrite or organic sulphur).

Within the limestone aquifer the concentrations and isotopic composition of sulphate may be further modified. Where the aquifer rocks contain diagenetic pyrite, this may oxidize to produce sulphate by reaction (1). This is a major source of sulphate in some aquifers (e.g. the Lincolnshire Limestone, eastern England; Moncaster *et al.* 1991). In the Castleton karst aquifer the sulphide minerals galena ( $\text{PbS}$ ) and sphalerite ( $\text{ZnS}$ ) are present in the mineral-vein 'rakes' which are believed to form the conduits for flow of allogenic waters from the sinks to Speedwell Cavern. Oxidation of these minerals could provide a source of sulphate within the aquifer in addition to the oxidation of disseminated diagenetic pyrite. Conversely, where groundwaters become sufficiently reducing, BSR (reaction 2) may occur and can be recognized by its isotopic effects (e.g. Strebel *et al.* 1990).

## SAMPLES AND METHODS

### *Strategy and rationale*

The study described here is based on a series of samples collected in an attempt to characterize isotopic compositions of sources and the nature of any sinks for sulphur in the catchment and to assess their relative importance. Three sets of samples were collected in late spring/early summer at times of relatively low stream flows as this provides the closest to a stable equilibrium between inputs to and outputs from the aquifer. A fourth set was collected under much higher stage in January 1996. Transit times for allogenic waters from sinks along solutionally enlarged conduits to risings in Speedwell cavern and on to the Castleton springs range from *c.* 50 h during flood events to over 240 h under drought conditions (Gunn, 1991), so samples collected on the same or following days should closely represent instantaneous input and output. Residence times in the unsaturated zone are longer (days to several tens of days; Bottrell and Atkinson, 1992) and we assume that percolation inflows sampled at Speedwell Cavern on the same day are representative of the limestone sector of the catchment. Rainfall was collected near the centre of the catchment area and sulphate derived by pyrite oxidation in the Namurian sequence was sampled at the high concentration springs described by Vear and Curtis (1981). Waters from the sub-catchments with significant sinking streams were sampled on four occasions to constrain sulphate sources within each and the composition of allogenic inputs to the aquifer. Aquifer waters were sampled on the same four occasions at the two major risings in Speedwell Cavern (MR, WR) and at high-level inlets tapping only autogenic percolation water (CC, BP). Aquifer waters were also sampled on one occasion from a private supply borehole at Oxlow House Farm (OX) and from the combined flow of the springs from which the catchment discharges (CS). Sediment samples from the main

groundwater conduits were collected in Speedwell Cavern itself and by cave divers from within the Main Rising sump (by J. Cordingley) and the P8 sumps (by P. Murphy).

### Field sampling

Water samples were collected from various sites in the catchment both above and below ground, as described above. Samples from sinks and risings were taken from as close as possible to the points of submergence and emergence, respectively. Samples for isotope and anion analysis were collected in 1000 ml plastic bottles which had previously been washed in dilute hydrochloric acid and distilled water. The bottles were rinsed twice with the sample water itself, taking care to deposit the washings well away from the sampling point, before being filled. Samples for cation analysis were taken in 50 ml plastic bottles which had been acid washed with dilute hydrochloric acid and distilled water and contained hydrochloric acid (50 per cent v/v, 5 ml) for sample preservation. Each sample was added to the bottle via a syringe filter using 0.45  $\mu\text{m}$  cellulose nitrate membrane filters which were preflushed with sample. In addition, a rain collector was erected with the water being collected from a funnel 1.1 m above ground (to prevent splash-back contamination) equipped with spikes to deter birds. The water was collected in pre-cleaned 5 l plastic bottles wrapped in light-proof black plastic to inhibit algal growth and containing a few millilitres of acidified copper nitrate solution as a biocide.

Table I. Anion and sulphate sulphur isotopic analyses

Site/date*	Sample type†	SO <sub>4</sub>	Cl	NO <sub>3</sub>	$\delta^{34}\text{S}$
P1-3	S	18.1	16.4	9.6	-1.7
P1-4	S	77.2	13.3	10.8	-7.9
P2-4	S	51.2	17.1	16.4	-5.3
P6-1	S	22.0	—	—	2.3
P6-2	S	20.5	25.6	4.7	1.2
P6-3	S	21.6	24.1	20.1	1.9
P6-4	S	52.2	25.3	24.0	-4.3
P7-1	S	22.0	—	—	1.1
P8-1	S	17.0	—	—	6.9
P8-2	S	6.7	9.8	0	11.3
P8-3	S	8.9	19.4	8.7	11.8
P8-4	S	6.1	18.2	15.5	-2.1
P12-4	S	71.2	27.2	10.8	-8.3
MR-1	R	25.0	—	—	1.4
MR-2	R	23.4	20.8	10.7	-1.0
MR-3	R	34.8	24.3	11.1	1.4
MR-4	R	80.1	17.6	—	-5.4
WR-2	R	17.9	6.5	4.0	2.8
WR-3	R	19.0	8.3	5.6	1.1
WR-4	R	17.9	8.5	7.9	1.6
CC-1	A	22.0	—	—	1.7
CC-2	A	20.0	7.6	8.6	0.8
CC-3	A	22.1	9.7	10.2	3.7
CC-4	A	19.6	11.7	17.4	1.8
BP-2	A	28.5	19.4	30.8	3.2
OX-2	A	29.0	21.2	10.9	0.1
CS-2		25.1	20.7	10.5	2.6
MT-1		1570	38	—	29.3
RW-A	RW	11.1	5.7	—	0.7
RW-B	RW	7.0	7.3	—	4.2
RW-C	RW	15.1	17.2	—	4.4
RW-AV‡	RW	11.08	11.92	—	4.05

\* Dates are given by suffix: 1 = May 1991; 2 = May 1995; 3 = October 1995; 4 = January 1996. RW-A, -B and -C are samples of bulk rainfall covering a one-year period; CS-2 is the combined waters of springs rising at Castleton; MT-1 is the spring in the shale sequence on Mam Tor

† S, sinking stream; R, conduit rising in Speedwell Cavern; A, autogenic catchment groundwater; RW, rainwater

‡ Annual average rainfall composition. Anion data are volume-weighted; isotopic data are weighted by sulphur mass

Agricultural intensity within the catchments studied was assessed by land-use survey and monitoring of agricultural operations on two separate occasions as part of this and other studies.

### Analysis

Measurements of pH, temperature and conductivity were taken *in situ*. Titratable alkalinity was also measured, using a Hach field titration kit. Water samples were analysed for anion concentrations (Cl, SO<sub>4</sub>, NO<sub>3</sub>) using a Dionex DX-100 ion chromatograph. For the isotopic analysis, barium sulphate was precipitated from each sample at a pH of 3 and 70°C by addition of an excess of BaCl<sub>2</sub>. This was converted to SO<sub>2</sub> gas using the method of Halas *et al.* (1982). Metal sulphide was extracted from sediment samples by reduction to H<sub>2</sub>S and precipitation as CuS (Newton *et al.*, 1995) which was combusted to SO<sub>2</sub> with Cu<sub>2</sub>O (Robinson and Kusakabe, 1975). Sample gases were purified by standard vacuum line cryogenic techniques for analysis on a VG Isogas SIRA 10 gas source mass spectrometer. Isotopic ratios are given in delta notation relative to the CDT international standard according to:

$$\delta^{34}\text{S}_{\text{sample}} = [(R_{\text{sample}} - R_{\text{CDT}})/(R_{\text{CDT}})] \times 1000 \quad (3)$$

where  $R = {}^{34}\text{S}/{}^{32}\text{S}$  ratio of the sample or standard.

## RESULTS

The results of surveys of agricultural activities are reported in detail elsewhere (Hardwick, 1995; Tranter *et al.*, 1996). Agricultural intensity in the allogenic catchments sampled in Rushup Vale increases in the order P1<P6<P8; autogenic catchments on the limestone are dominantly used for low intensity sheep farming and are unimproved or semi-improved grazing land.

The chemical and isotopic data on all water samples are reported in Table I. The rainwater input varies between summer (RW-1; SO<sub>4</sub>/Cl = 1.95,  $\delta^{34}\text{S}$  = 0.7 per mil) and autumn/winter (RW-2 and RW-3; SO<sub>4</sub>/Cl = 0.96 and 0.88,  $\delta^{34}\text{S}$  = 4.2 and 4.4 per mil). This is consistent with a dominance of isotopically light sulphur from fossil-fuel burning with no associated chloride in the summer and a larger contribution of sea-water derived sulphate aerosol at +20 per mil with associated chloride in the stormier autumn/winter months (see Bottrell and Novak, 1997). The mass-averaged rainfall composition is given in Table I. Within the surface catchment, sulphate concentration may increase due to a variety of processes and most of the waters analysed exhibit an increase in sulphate concentration above rainwater. The springs in the sandstone–shale sequence at Mam Tor (MT-1, Table I) have very high (1570 mg l<sup>-1</sup>) sulphate concentrations from pyrite oxidation (Vear and Curtis, 1981); the rainwater sulphate is insignificant and the sulphate isotopic composition of –29.3 per mil is representative of the pyrite source (since oxidation to sulphate involves negligible isotopic fractionation; Nakai and Jensen, 1964; Toran and Harris, 1989). At low stage, waters draining the P6 and P7 catchments are also enriched in sulphate relative to rainwater but to a lesser extent (SO<sub>4</sub> = 20.5 to 22.0 mg l<sup>-1</sup>) and have isotopic compositions only slightly lighter than rainwater (+1.1 to +2.3 per mil). The P1 sample also has increased SO<sub>4</sub> concentrations but lighter isotopic compositions (18.1 mg l<sup>-1</sup> at –1.7 per mil). The P8 catchment is rather different, having much lower sulphate concentrations (6.7 to 17.0 mg l<sup>-1</sup>), some of which are even lower than the rainwater inputs, and much heavier isotopic compositions (+6.9 to +11.8 per mil). The percolation waters sampled in the limestone catchment are enriched in sulphate relative to rainfall (20.0 to 28.5 mg l<sup>-1</sup>) and have a spread of isotopic compositions again toward lighter values than the rainfall input (–3.7 to +3.2 per mil). On the four occasions sampled, the waters at Main Rising and Whirlpool Rising were always distinct in both (at least some aspects of) their chemistry and their sulphate isotopic composition.

Sulphur isotopic analyses were also made on sulphide minerals in sediment samples from the cave systems (Table II). The values obtained (–4.4 to –5.6 per mil) are in the same range as the ore sulphide minerals galena (PbS) and sphalerite (ZnS) in the mineralized rakes of this catchment, reported by Robinson and Ineson (1979) and Ewebank *et al.* (1995). Indeed, sample SPW-7C and other sediment samples from Speedwell Cavern have high Pb and Zn concentrations (Bottrell *et al.*, 1999) and sulphide minerals from the

Table II. Isotopic analyses of sulphide in sediments and rocks

Sample ID	Sample type	Sulphidic S (wt%)	$\delta^{34}\text{S}$ (‰ CDT)
P8-S1	Sump 9, P8 cave	0.35	−4.4
MR-Sed.	Main Rising Sump, Speedwell Cavern	0.03	−5.6
SPW-7C	Far Canal, Speedwell Cavern	0.02	−4.9
ML-1	Bee Low Limestone	0.014	−22.3
ML-2	Bee Low Limestone	0.010	+3.4
SMQ-E	Bee Low Limestone	0.133	−15.8
SMQ-G	Bee Low Limestone	0.046	−19.1
SMQ-J	Bee Low Limestone	0.034	−17.0

rakes are therefore likely to be the dominant contributor to the sediments, since pyrite from the Namurian catchments (which might be transported in detrital material from the surface catchments into the stream-sinks, especially in flood) has far lighter isotopic compositions (see above). A number of limestone samples were also analysed for pyrite sulphur. Those from the light facies contain too little S for isotopic analysis, but CuS was recovered from samples of dark facies limestone which contained more S (0.010–0.133 weight per cent) but had variable isotopic composition (+3.4 to −22.3 per mil, but with most samples giving isotopically light values; Table II) dependent on their original depositional and diagenetic environment.

## DISCUSSION

### *Surface stream catchments*

*Baseflow data (Figure 2, visits 1, 2 and 3).* The catchments examined show a range of sulphate concentrations and isotopic compositions. Any increases in sulphate concentration in the surface catchments could be due (in part) to evapotranspiration, which increases the concentration of all solutes. Usually chloride is used as a conservative ion and ratios of sulphate to chloride, which should be unaffected by evapotranspiration, are given in Table III. For the P1, P6 and P7 catchments on Namurian/Quaternary deposits, increase in  $\text{SO}_4$  concentration relative to rainwater is accompanied by a decrease in  $\text{SO}_4/\text{Cl}$ , so chloride must have been added in greater proportion relative to sulphate. This is probably from agricultural sources (slurries and fertilizers containing chloride in greater proportion to sulphate than rainwater; Tellam *et al.*, 1994); indeed  $\text{SO}_4/\text{Cl}$  correlates well with agricultural intensity in each catchment (intensity

Table III. Sulphate/chloride ratio of water samples

Site	Visit 2	Visit 3	Visit 4
P1	—	1.104	5.805
P2	—	—	2.994
P6	0.802	0.896	2.063
P7	—	—	—
P8	0.684	0.459	3.352
P12	—	—	2.618
MR	1.125	1.432	4.551
WR	2.631	2.289	2.106
CC	2.632	2.278	1.675
BP	1.469	—	—
CS	1.213	—	—
OX	1.368	—	—
RW	A : 1.947	B : 0.959	C : 0.878

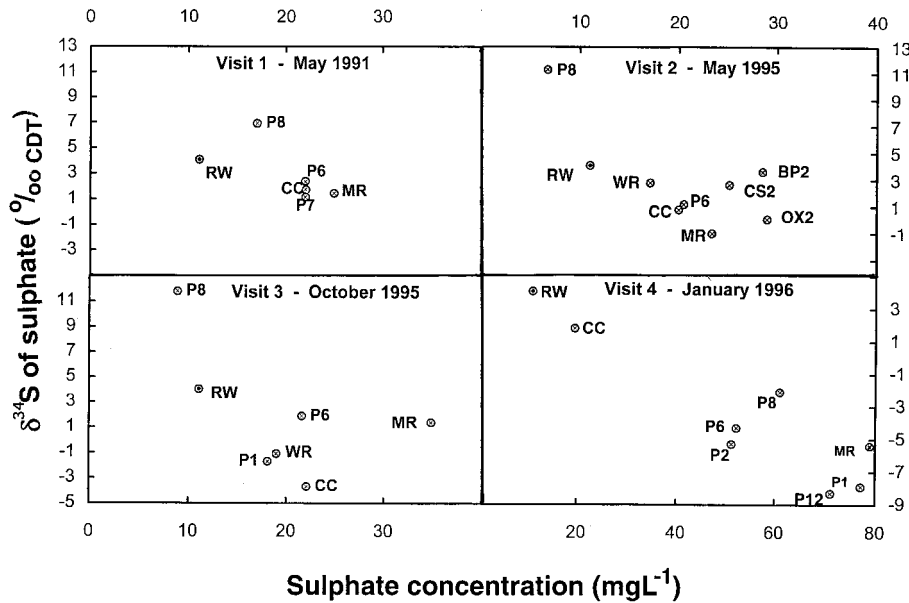


Figure 2. Sulphate sulphur isotopic compositions of rain, surface streams and waters sampled in Speedwell cavern. Note that scales change between figures but the same annual average rainwater composition (RW) is plotted on each figure

P1 < P6 < P8;  $\text{SO}_4/\text{Cl}$  P1 > P6 > P8). As well as increasing in concentration, sulphate–sulphur isotopic composition changes between rainwater and streamwaters, which we interpret as being due to addition of some sulphate. The isotopic composition of the sulphate added differs between the P1 and P6/P7 catchments, P1 having significantly lighter sulphate. Whilst the headwaters of these catchments lie on Namurian shales which could supply isotopically light sulphate from pyrite oxidation, this would lead to increased  $\text{SO}_4/\text{Cl}$  compared to rainwater, which is not the case. The low  $\text{SO}_4/\text{Cl}$  of these waters and its correlation with agricultural intensity indicate that agricultural sources must dominate in P6/P7; most sulphate isotopic compositions in these two catchments are around +1 to +2 per mil consistent with a sulphate source from NPK fertilizers (+1 to +3 per mil) and animal slurries (+4 to +6.4 per mil) (data from Tellam *et al.*, 1994). In P1, higher  $\text{SO}_4/\text{Cl}$  and lighter sulphate–sulphur isotopic composition probably relates to lower agricultural inputs here and thus a more significant signal from pyrite oxidation.

The data from the P8 catchment initially appear somewhat incongruous. This is the most intensively farmed catchment in the study area and receives the highest input of fertilizers and slurries. However, sulphate concentrations and  $\text{SO}_4/\text{Cl}$  in the streamwaters draining this catchment are consistently extremely low (both often lower than rainwater) and the sulphate sulphur is strongly enriched in  $^{34}\text{S}$ . Given that the agricultural sulphate inputs to this catchment are as large or larger than for P6 and P7, then sulphate must be being removed at some point; this is most likely due to bacterial sulphate reduction and fixing of sulphur as sulphide in the soil zone. The sulphide fixed will be depleted in  $^{34}\text{S}$  as a result of the bacterial process, leaving decreased concentrations of  $^{34}\text{S}$ -enriched sulphate, as observed. If the P8 catchment waters had initial compositions close to the P6 and P7 waters, then bacterial reduction has removed 25–70 per cent of the sulphate and imposed an isotopic enrichment factor ( $\epsilon$ ) of 8–21 per mil (Table IV), consistent with the range usually encountered with sulphate-reducing bacteria (Chambers and Trudinger, 1979). The dominance of this process in this catchment is probably a direct result of modification of the soil zone redox chemistry by large inputs of organic matter as slurry (e.g. McCarthy and Bottrell, 1999).

*High stage data (Figure 2, visit 4).* Under high stage the sinking streams have higher sulphate concentration,  $\text{SO}_4/\text{Cl}$  much greater than rainfall and much lighter isotopic composition. This additional

Table IV. Isotopic enrichment factors required during Rayleigh fractionation on removal of sulphate from P6/P7 waters to generate P8 compositions

Site	SO <sub>4</sub> (mg l <sup>-1</sup> )	δ <sup>34</sup> S (‰ CDT)	SO <sub>4,REM</sub> *	ε†
P8-1	17.0	+6.9	77.3	-21
P8-2	6.7	+11.3	30.5	-8
P8-3	8.9	+11.8	53.6	-16

\* Sulphate concentration of the P8 catchment as a percentage of the average values of P6 and P7 (22 mg l<sup>-1</sup> and +1.5 per mil)

† Isotopic enrichment factor calculated for Rayleigh fractionation during removal of sulphate from average P6/P7 water to generate observed composition of P8 water.  $\epsilon = 10^3 \ln \alpha$

source of sulphur, which we take to be isotopically light sulphate from pyrite oxidation stored in soil moisture, is being washed in from the catchment headwaters on the Namurian shales of Rushup Edge.

#### *Autogenic catchment (Figure 2)*

Autogenic inputs to groundwater were sampled as percolation inflows to the cave system (CC, BP) and at a water supply borehole in the limestone at Oxlow House Farm (OX). These samples will thus reflect a combination of inputs to the catchment as rainfall plus any agricultural sources and the effects of any processes operating in the soil and unsaturated zones. The data for these waters exhibit a wide spread, but all show increased sulphate concentration and SO<sub>4</sub>/Cl relative to the rainwater input (Table III). All the percolation waters have δ<sup>34</sup>S values lighter than rainwater sulphate. These isotopic compositions are similar to those in the P6 and P7 catchments and could derive from similar agricultural inputs. However, agricultural intensity is lower in the autogenic catchments on limestone, and SO<sub>4</sub>/Cl is higher in the percolation waters; both of these factors suggest that a different sulphate source, not associated with chloride, is involved. This could be oxidation of sulphide minerals in ore veins (δ<sup>34</sup>S = -4 to -10 per mil) or oxidation of diagenetic pyrite in the limestone matrix which has variable δ<sup>34</sup>S but also provides a source of isotopically light sulphur (see above). This is consistent with results from studies of New Zealand rivers by Robinson and Bottrell (1997) who found that in low agricultural intensity catchments, rainfall inputs and rock weathering dominated sulphate isotopic compositions.

The CC-3 sample is then something of an anomaly, exhibiting a far larger shift in δ<sup>34</sup>S relative to rainwater. One possibility is that, since the third sampling took place after a long period of drought (during which the Boulder Piles percolation inlet dried up totally), the very much reduced flow of Cliff Cavern (CC) is dominated by a long residence time component which is insignificant at higher flows. Studies of mixing and storage in a similar Carboniferous limestone aquifer in Yorkshire, UK (Bottrell and Atkinson, 1992), show that, while a majority of recharge passes through the unsaturated zone in < 72 h, there is significant storage with a residence time of several tens of days or longer. Since CC-3 was collected after 20 weeks of abnormally low rainfall, this sample must represent the small component of very long residence time storage of the unsaturated zone. As such, it will have undergone a significant degree of interaction with the limestone and an additional component of isotopically light sulphur may well be derived by oxidation of diagenetic pyrite in the limestones.

#### *Waters rising in Speedwell Cavern and Castleton (see Figure 2)*

Waters rising at Speedwell Main Rising (MR) are always enriched in sulphate and SO<sub>4</sub>/Cl (Table I and III) relative to the sinking streams at Perryfoot, so sulphate has been added during transit from sink to resurgence. Though the dominant flow can switch between Main and Whirlpool Risings in Speedwell (Bottrell and Gunn, 1991), the dominant flow was always from MR when samples for this study were collected. Hence these samples will be composed largely of the allogenic stream waters. The addition of sulphate between the stream sinks and MR is accompanied by a change in sulphate sulphur isotopic composition. The data are summarized in Table V. Because the amount of sulphate added in the transit from sinks to MR can be estimated and the



Table V. Calculation of composition of sulphate added between sinks and resurgence at Speedwell Main Rising

Visit	Sinking Stream		Main Rising		SO <sub>4,XS</sub> * (mg l <sup>-1</sup> )	δ <sup>34</sup> S <sub>XS</sub> † (‰ CDT)
	Mean SO <sub>4</sub> (mg l <sup>-1</sup> )	Mean δ <sup>34</sup> S (‰ CDT)	Mean SO <sub>4</sub> (mg l <sup>-1</sup> )	Mean δ <sup>34</sup> S (‰ CDT)		
1	20.3	+3.1	25.0	+1.4	4.7	-5.9
2	15.2	+4.5	23.3	-1.0	8.1	-11.3
3	16.2	+2.4	34.8	+1.4	18.6	+0.5
4	62.6	-5.8	80.1	-5.4	17.5	-4.0

\* Concentration of sulphate added, Equation 5 of text

† Isotopic composition of sulphate added, Equation 4 of text

isotopic composition of the sinking streams has been measured, the isotopic composition of the source of sulphate added (δ<sup>34</sup>S<sub>XS</sub>) can be calculated by isotopic mass balance:

$$\delta^{34}\text{S}_{\text{MR}} \times [\text{SO}_4]_{\text{MR}} = \delta^{34}\text{S}_{\text{SINK}} \times [\text{SO}_4]_{\text{SINK}} + \delta^{34}\text{S}_{\text{XS}} \times [\text{SO}_4]_{\text{XS}} \quad (4)$$

where [SO<sub>4</sub>]<sub>SINK</sub> and δ<sup>34</sup>S<sub>SINK</sub> are approximated as the weighted means of P1, P2, P6, P7, P8 and P12 catchment concentration and isotopic data, respectively (where no data are reported there was insufficient flow for sampling), and:

$$[\text{SO}_4]_{\text{XS}} = [\text{SO}_4]_{\text{MR}} - [\text{SO}_4]_{\text{SINK}} \quad (5)$$

The calculated values of δ<sup>34</sup>S<sub>XS</sub> are given in Table V and range from 0.5 per mil to -11.3 per mil. There are two possible sources for this sulphate:

- (1) Mixing of high sulphate concentration autogenic waters with the allogenic waters during the sink to rising transit (e.g. the OX-2 and BP-2 waters, Figure 2).
- (2) Oxidation of galena and sphalerite ore minerals from the mineralized rakes by the allogenic waters.

Whilst there is clearly a proportion of autogenic water at the rising (the importance of which will vary with discharge), the isotopic data preclude autogenic waters with high sulphate concentration (as sampled at BP-2 and OX-2, Figure 2) as the dominant source of the additional sulphate. The calculated isotopic composition of the sulphate added between sinks and MR (Table V) is generally isotopically lighter than the sulphate in percolation waters (Table I).

The range of isotopic compositions of the common sulphide minerals for the veins in the Castleton catchment ranges from -4 to -10 per mil (Robinson and Ineson 1979; Ewebank *et al.*, 1995), a similar range to the calculated additional sulphate component (Table V), and the sulphide in sediments from the system also falls into this range (Table II). This demonstrates that the dominant source of the increased sulphate in the MR waters is oxidation of ore sulphide minerals. Even though two of the sediment samples for sulphide analysis were taken in the sumps and upstream of all lead workings in Speedwell, it is possible that some ore minerals could be derived from old workings on the Coalpithole Rake at Perryfoot. However, Bottrell *et al.* (1999) report elevated Ba, Pb and Zn concentrations in ancient (certainly pre-mineworking) sediment in Speedwell Cavern, indicating that abrasion and/or reaction of ZnS and PbS has taken place as an entirely natural phenomenon.

Using the excess sulphate concentrations from Table V and taking the average discharge at MR to be 100 l s<sup>-1</sup>, the flux of sulphate derived from ore mineral oxidation can be calculated as 12.5 tonnes/year (t a<sup>-1</sup>). The mineralized rakes in the catchment total c. 5 km length and are generally c. 2 m wide. Assuming weathering over a 200 m zone between surface and base-level, and that 5 per cent of vein volume is galena, gives 0.75 Mt galena (= 0.1 Mt S). At present rates this would be removed in 8000 years and doubling the estimate to

include mineralization in possible minor side veins and pipes in country rock would still yield only enough S to sustain weathering for 16 000 years at present rates. It is most likely that mining activity has modified sulphide oxidation rates, not by lowering of groundwater heads (which are still controlled by natural sumps), but by providing sulphidic mine waste and debris with an artificially high surface area for oxidation.

The waters from WR in Speedwell Cavern are always distinct from those of MR, both in terms of sulphate concentration (being lower than MR on any given occasion, Table I) and in terms of isotopic composition, being distinctly heavier on the second and fourth sampling and lighter on the third (Figure 2). These two waters must then have different catchments. It is noteworthy that between the second and third sampling visits the WR sulphate became depleted in  $^{34}\text{S}$  to almost exactly the same extent as the CC water discussed above, and on the fourth occasion, when the allogenic waters were all isotopically light, the WR composition remained close to that of autogenic percolation inflow to CC. Whilst WR can be the main resurgence for the allogenic waters under some conditions (Bottrell and Gunn, 1991), under conditions of only minor discharge from WR, the largest component of the WR water is derived in large part from autogenic inflows similar to those at Cliff Cavern.

Between sinking again in Speedwell Cavern and our sampling point at Castleton (CS), the MR+WR waters are augmented by autogenic waters from the Peak Cavern Rising. Thus on Figure 2 the CS-2 sample lies away from a line linking MR-2 and WR-2 (along which any mixture of these waters would lie), and the displacement is towards the composition of the BP-2 percolation inflow, suggesting that the autogenic waters added have a similar composition (i.e. derived from rainfall and rock weathering inputs).

## CONCLUSIONS

Sulphur isotopic compositions of sulphate are an effective tool for establishing sulphur sources and processes acting within a catchment. Effects of agrichemical additions and sulphate reduction arising from slurry application can be distinguished from rock weathering reactions. In the Castleton karst, groundwater flowing in conduits on mineralized faults gains sulphate from oxidizing ore sulphide minerals and mass balance considerations show that current rates of ore sulphide oxidation are enhanced by the effects of mining. Percolation waters are dominated by sulphate from rainfall and weathering of diagenetic pyrite in the limestones.

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